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Exploring Chromophore Tethered Aminoethers as Potential Photoinitiators for Controlled Radical Polymerization

by

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Exploring chromophore tethered aminoethers as potential photoinitiators for controlled radical polymerization

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Abstract

Compounds **1–4** containing various light absorbing chromophores attached covalently to a hindered aminoether (2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) aminoether) were synthesized, and their photochemistry and photophysics studied in an attempt to develop photoinitiators for radical "living" polymerization. Significant shortening of the chromophore's triplet lifetime was observed in **1–4** as compared to analogous compounds containing no alkylated TEMPO moiety, which suggests an intramolecular quenching of the excited chromophore by the aminoether functionality. The efficiency of the quenching process depends on the chromophore. Employing **1–4** as unimolecular photoinitiators for styrene "living" polymerization was proven to be difficult due to rapid quenching of the excited state of the initiator by this monomer. Compound **4** was demonstrated as an initiator for controlled photopolymerization of methyl methacrylate. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Photoinitiator; Controlled polymerization; Photosensitization

1. Introduction

It has been established that 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) traps a wide range of free radicals at rate constants close to the diffusion control limit [1–3]. Employing this chemistry, Georges et al. demonstrated that free radical polymerization of styrene in the presence of TEMPO results in a polymer with low polydispersity [4–8]. The rapid trapping of the growing polymer chain by TEMPO and the thermal reversion of this process is pivotal to the living polymerization mechanism as shown in Scheme 1. Reaction (1) represents the reversible reaction between the polymeric radical and TEMPO. The equilibrium depicted in (1) exists at a certain temperature such that a steady state is reached where a small amount of TEMPO is present in the reaction system. Repeating reactions (1) and (2) results in longer polymer chains and an increase in the molecular weight of the resulting polymer products. The rapid trapping of $[M]_n\cdot$ by TEMPO leads to low concentrations of the propagation radicals [9], thus avoiding the normal termination reactions such as that described in reaction (3). Elimination of the uncontrollable termination processes results in polymers with narrow molecular weight distribution, and realizes the concept of "living" free radical polymerization [10].

Hawker et al. studied alkylated TEMPO's of general structure $\mathbf{G_1}$ (Scheme 2) as unimolecular initiators for "living" radical polymerization [11–15]. Thermolysis of $\mathbf{G_1}$ delivers a benzylic radical which succeeds in initiating the polymerization reaction and a TEMPO radical that controls the concentrations of the propagating radicals. Compared to the bimolecular systems described in Scheme 1, Hawker's unimolecular initiators afforded even better control over the molecular weight and polydispersity for the resulting polymer [12]. However, the above-mentioned polymerization reactions were all executed thermally and generally required long reaction times at relatively high temperatures, which limits wider applications of this technology and causes problems under certain conditions (such as autopolymerization of styrene, etc.). In an effort to eliminate these problems, we became interested in developing analogous "living" polymerization systems using photochemical methods.

In a similar attempt, intermolecular photosensitized decomposition of aminoethers like $\mathbf{G_1}$ was investigated by Scaiano et al. who employed different sensitizers [16]. However, the efficiency of this intermolecular process was low, and the expected cleavage of the targeted C–O bond

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$$[M]_n\cdot + \text{TEMPO} \underset{k_{-t}}{\overset{k_t}{\rightleftharpoons}} [M]_n\text{-TEMPO} \quad (1)$$

$$[M]_n\cdot + [M] \xrightarrow{k_p} [M]_{n+1}\cdot \quad (2)$$

$$[M]_n\cdot + [M]_p\cdot \xrightarrow{k_T} [M]_{n+p} \quad (3)$$

Scheme 1.

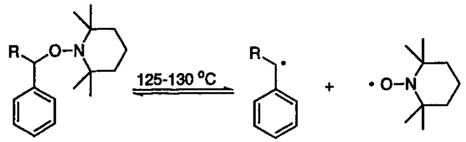
was not always observed. Hoping to realize the photoinduced "living" polymerization, we designed and synthesized compounds of general structure **G**$_2$ (Scheme 3), where different chromophores were covalently connected to the TEMPO moiety. Analogous to the thermal counterpart **G**$_1$, it was expected that the intramolecular sensitization in **G**$_2$ would induce the C–O bond homolysis and furnish a TEMPO radical as well as a benzylic radical and that **G**$_2$ can serve as an unimolecular photoinitiators for "living" radical polymerization.

Other researchers have also investigated possible routes to control photopolymerization reactions. Photochemically-generated sulfur-centered radicals were shown to react reversibly with growing polymer chain ends and different "iniferters" were employed to invoke a controlled polymerization process [17]. A recent report indicates the sulfur-centered radicals can be employed as molecular weight controllers in photopolymerizations of methyl methacrylate [18].

2. Experimental section

2.1. Material

Benzene (Aldrich) was distilled over sodium benzophenone ketyl under argon. Other chemicals obtained from commercial sources were used as received. NMR spectra were taken either on a Varian Gemini 200 NMR spectrometer or a Varian Unity Plus 400 NMR spectrometer using chloroform-*d* as solvent. Chemical shifts in ^{1}H NMR are in ppm with TMS as the internal standard (0 ppm) and those in ^{13}C NMR are referenced against the center peak of chloroform-*d* (77.0 ppm). Routine GC measurements were carried out on a Hewlett-Packard(HP) 5890 Gas Chromatograph with a 30 m × 0.253 mm ID × 0.25 μm film thickness DB-1 column (J&B Scientific) and a flame ionization detector. GC/MS were taken on Hewlett-Packard 5988 mass spectrometer coupled to an HP 5880A GC with a 30 m × 0.25 mm ID × 0.25 μm film thickness DB-5 ms column (J&B Scientific), interfaced to an HP 2623A data processor. Infrared spectra were taken with a Galaxy™ series 6020 FTIR Spectrometer. Thin layer chromatography was performed with Whatman® silica gel coating TLC plates. Silica gel (60 Å, 60–200 mesh) was used in column chromatography. Melting points were determined with a Thomas Hoover capillary melting point apparatus and were uncorrected. UV absorption spectra were recorded on an HP 8452A diode-array UV/Visible spectrophotometer. Gel permeation chromatography was performed with an HP 1050 series HPLC equipped with an HP 1047A refractive index detector and a PLgel 5 μm mixed-C 300 × 7.5 μm column. HPLC grade THF was used as eluent. Polyacrylate standard samples were obtained from Scientific Polymer Products, Inc.



G$_1$

Scheme 2.

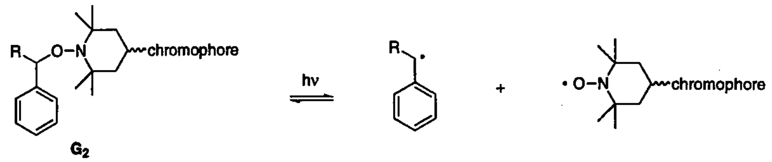
2.2. Time resolved laser flash photolysis

Nanosecond laser flash photolysis was carried out on a setup described by Ford and Rodgers [19] using the third harmonic of a Q-switched Nd:YAG laser as the excitation source. The sample solution in a quartz cuvette was purged by argon for 10 min before and continuously during the experiment. The samples were excited with 355 nm pulses (pulse width ca. 7 ns).

1-Benzyloxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (**5**) [15] and 1-hydroxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (**6**) [20] were prepared according to the literature procedures.

1-(4′-Benzoyl)benzyloxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (**1**): To a mixture of alcohol **6**,4-benzoylbenzoic acid, and 4-*N*,*N*′-dimethylaminopyridine (molar ratio: 1.0:1.1:0.1) in a round bottom flask, dry dichloromethane was added to make an approximately 0.2 M solution. The solution was then placed over ice and cooled to 0°C. An equal molar amount of 1,3-dicyclohexylcarbodiimide (DCC) in dry dichloromethane was added dropwise to the stirred solution. Usually, a white precipitate formed instantly. The mixture was then allowed to warm to room temperature and stirred overnight. The precipitate was filtered off and the solvent evaporated in vacuo. Purification by flash column chromatography using hexanes (H): ethyl acetate (EA) (10:1) as eluents produced **1** as a clear oil in about 90% yield. R_f in H:EA (10:1) = 0.22; ^{1}H NMR (200 MHz) δ 0.76 (s, 3H), 1.07 (s, 3H), 1.20 (s, 3H), 1.37 (s, 3H), 1.28–1.56 (m, 6H), 4.57 (dd, $J_1 = 5.8$ Hz, $J_2 = 11$ Hz, 1H), 4.86 (dd, $J_1 = 5.8$ Hz, $J_2 = 11$ Hz, 1H), 5.08 (t, $J = 5.8$ Hz, 1H), 7.03–7.62 (m, 8H), 7.79 (d, $J = 8.4$ Hz, 4H), 8.02 (d, $J = 8.4$ Hz, 2H); IR (cm^{-1}) 2932, 1732, 1667, 1082.

1-Phenyl-1-(4′-hydroxy-2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy) ethane (**7**) was prepared employing a modified literature method [21,22]. A Pyrex® test tube was charged with 300 mg 4-hydroxy-TEMPO, 1.0 g *tert*-butyl peroxide, and 15 ml of freshly distilled anhydrous ethylbenzene. The solution was degassed by purging with dry argon for 30 min and then irradiated at room temperature in a Rayonet RPR-100 photoreactor equipped with 16 350 nm GE® F8T5 BLB



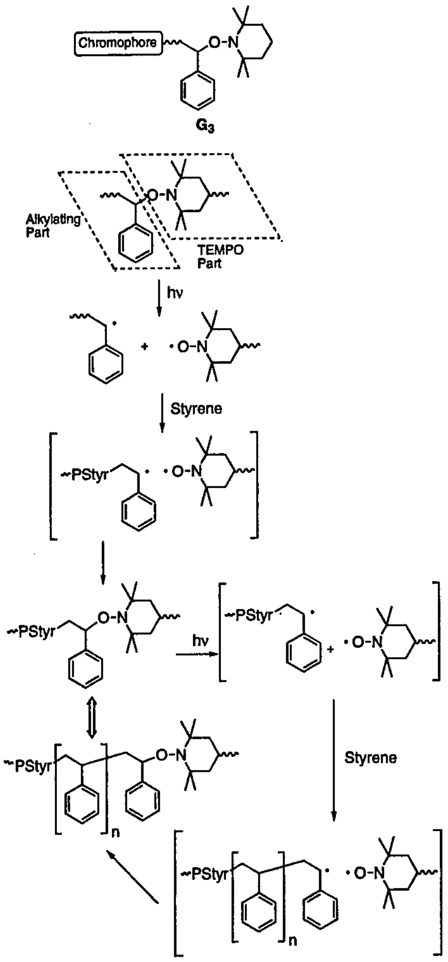
Scheme 3.

UV lamps. The reddish color due to the TEMPO starting material disappears in 2–3 hrs indicating the reaction is complete. The solution was washed with sodium thiosulfate (10%) and brine and dried over $MgSO_4$. Removal of the ethylbenzene solvent under reduced pressure followed by column chromatography over silica afforded **7** as a white solid in 59% isolate yield. Melting point 86–87°C. R_f in H:EA (3:1) = 0.25; ^{1}H NMR (200 MHz) δ 1.07 (s, 3H), 1.21 (s, 3H), 1.33 (s, 3H), 1.48 (d, $J = 7.0$ Hz, 3H), 1.56 (s, 3H) 1.54–1.87 (m, 5H), 3.94 (br, 1H), 4.77 (q, $J = 7.0$ Hz, 1H), 7.26–7.32 (m, 5H); ^{13}C NMR (50 MHz) δ 21.2, 23.4, 34.1, 34.4, 48.7, 48.8, 59.9, 60.1, 63.3, 83.3, 126.6, 126.9, 128.0, 145.4; IR (cm^{-1}) 3278, 29708, 8, 1374, 1090, 1048.

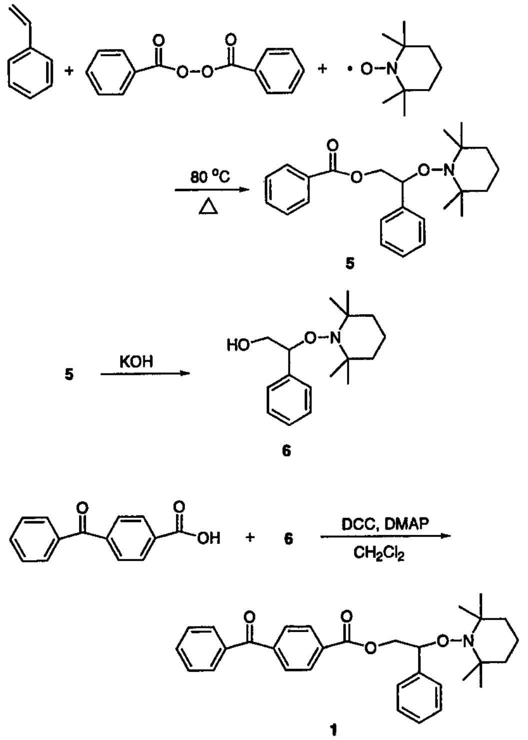
1-Phenyl-1-[4′-(4″-benzoyl)benzyloxy-2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy]ethane (**2**) was prepared in 85% yield using similar procedures as outlined for **1** starting with 4-benzoylbenzoic acid and **7**. ^{1}H NMR (400 MHz) δ 0.68 (s, 3H), 1.20 (s, 3H), 1.26 (s, 3H), 1.39 (s, 3H) 1.51 (d, $J = 7.0$ Hz, 3H), 1.61–1.93 (m, 5H), 4.81 (q, $J = 7.0$ Hz, 1H), 5.29 (m, 1H), 7.30–7.33 (m, 5H), 7.45–7.50 (m, 2H), 7.56–7.62 (m, 1H), 7.76–7.83 (m, 4H), 8.08–8.12 (m, 2H); ^{13}C NMR (100 MHz) δ 14.0, 21.1, 22.6, 22.8, 23.2, 25.2, 26.9, 31.5, 44.7, 68.1, 83.4, 126.6, 128.0, 128.4, 129.3, 130.0, 132.8, 133.7, 137.0, 141.2, 144.5, 145.2, 165.2, 195.8.

1-Phenyl-1-(4′-benzoylformyl-2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy]ethane (**3**) was prepared in 88% yield using similar procedures as outlined for **1** starting with benzoylformic acid and **7**. ^{1}H NMR (400 MHz) δ 0.66 (s, 3H), 1.18 (s, 3H), 1.26 (s, 3H), 1.37 (s, 3H) 1.50 (d, $J = 6.4$ Hz, 3H), 1.61–2.04 (m, 5H), 4.79 (q, $J = 6.4$ Hz, 1H), 5.31 (m, 1H), 7.21–7.25 (m, 1H), 7.29–7.31 (m, 4H), 7.47–7.51 (m, 2H), 7.61–7.65 (m, 1H), 7.96–7.98 (m, 2H); ^{13}C NMR (100 MHz) δ 14.0, 21.1, 22.6, 23.2, 31.6, 44.4, 60.0, 60.3, 69.7, 83.4, 126.7, 127.0, 128.1, 128.8, 129.9, 132.5, 134.7, 145.2, 163.6, 186.3.

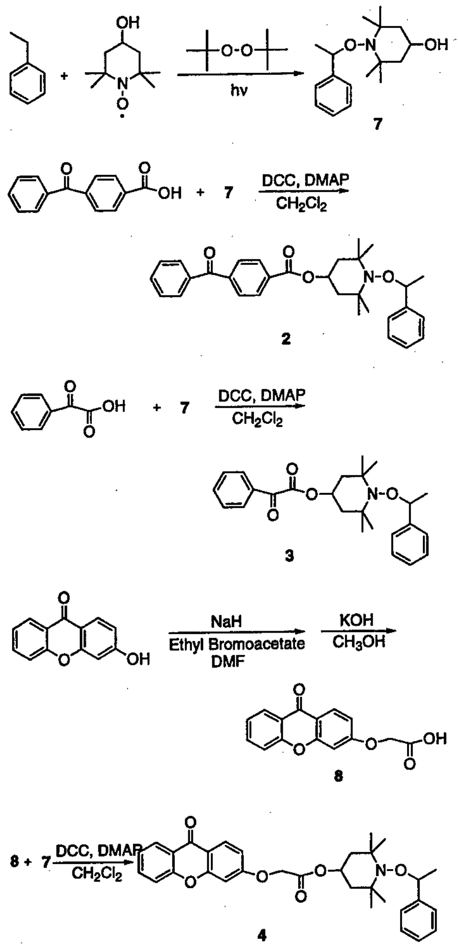
Xanthon-3-yloxyacetic acid (**8**) was prepared in 91% overall yield according to a modified literature procedure



Scheme 4.



Scheme 5.



Scheme 6.

as outlined in Scheme 6 beginning with 3-hydroxyxanthone [23].

1-Phenyl-1-[4′-(2″-xanthon-3‴-yloxyacetoxyl)-2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy]ethane (**4**) was prepared in 85% yield using similar procedures as outlined for **1** starting with xanthon-3-yloxyacetic acid (**8**) and **7**. White solid; Melting point 112–114°C. R_f in H:EA (5:1) = 0.25; ^{1}H NMR (200 MHz) δ 0.63 (s, 3H), 1.08 (s, 3H), 1.23 (s, 3H), 1.30 (s, 3H) 1.45 (d, $J = 6.6$ Hz, 3H), 1.52–1.98 (m, 5H), 4.67 (s, 2H), 4.73 (q, $J = 6.6$ Hz, 1H), 5.12 (m, 1H), 6.82 (d, $J = 2.2$ Hz, 1H), 6.93 (dd, $J_1 = 2.2$ Hz, $J_2 = 8.8$ Hz, 1H), 7.19–7.44 (m, 7H), 7.63–7.71 (m, 1H), 8.22–8.31 (m, 2H); ^{13}C NMR (50 MHz) δ 21.1, 23.3, 34.0, 34.3, 44.4, 59.9, 60.2, 65.5, 68.8, 83.4, 101.4, 113.0, 116.6, 117.7, 121.9, 124.0, 126.6, 127.0, 128.1, 128.6, 134.4, 145.2, 156.2, 157.7, 163.0, 167.5, 176.2; IR (cm^{-1}) 2976, 2930, 1760, 1660, 1621, 1610, 1465, 1211, 1092.

2.3. Photopolymerization procedures

Acetonitrile solutions containing 0.005 M of **4** and different amounts of methyl methacrylate were placed in Pyrex® test tubes and degassed by purging with dry argon for 20 min. Irradiation was carried out in the Rayonet reactor. Polymer products were collected by precipitating in methanol and drying to constant weight under vacuum.

3. Results and discussion

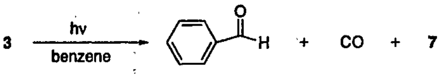
3.1. Design and synthesis

Based on earlier results of the intermolecular sensitized homolysis of the C–O bond in the alkylated TEMPO compounds [16], we surmised that an analogous intramolecular process would render more efficient C–O bond cleavage and better control over the polydispersity of the resulting polymer according to similar observations from the unimolecular thermal initiators [12]. A light absorbing chromophore can be attached to the alkylated TEMPO molecule in two different ways. One links the chromophore directly with the TEMPO portion of the molecule as in $\mathbf{G}_2$. The other attaches the chromophore to the alkylating part as in $\mathbf{G}_3$, Scheme 4. Employing the established synthetic route to alcohol **6**, we first synthesized a benzophenone containing alkylated TEMPO **1** pertaining to the general structure $\mathbf{G}_3$ [20]. The living polymerization mechanism shown in Scheme 1 was further illustrated in Scheme 4 for reactions employing unimolecular photoinitiators like $\mathbf{G}_1$ and $\mathbf{G}_3$. As the polymerization reaction proceeds, the chain length between the alkylating portion and the TEMPO portion of the initiator increases. If the chromophore is attached to the alkylating portion of the initiator such as in $\mathbf{G}_3$ (**1**), the distance between the chromophore and the targeted C–O bond increases with the polymerization reaction. Concerned that this situation will decrease the efficiency of the intramolecular sensitized C–O homolysis, we designed initiators of general structure $\mathbf{G}_2$ (**2–4**) where the chromophore is directly attached to the TEMPO portion of the molecule. As revealed in Scheme 4, the distance between the chromophore in $\mathbf{G}_2$ and the bond to be homolysized does not change with the progress of the polymerization reaction. Believing that $\mathbf{G}_2$ is a better design for the initiator than $\mathbf{G}_3$, we synthesized several compounds of this type containing different chromophores.

Compound **1** was synthesized according to Scheme 5. Alkylated TEMPO **5** was isolated from a benzoyl peroxide initiated polymerization reaction of styrene in the presence of the TEMPO radical. Hydrolysis of **5** produced **6** in high yield [20]. Esterification of **6** with 4-benzoylbenzoic acid furnished **1** in good yield. Synthesis of **2–4** was accomplished as shown in Scheme 6. Alcohol **7** was obtained by irradiating ethylbenzene in the presence of *tert*-butyl peroxide and 4-hydroxy-TEMPO [21,22]. Esterification of **7** with the chromophore containing carboxylic acids results in **2–4**, in high yields.

3.2. Photochemistry and photophysics

When benzene solutions (0.02 M) of **1–4** were irradiated,



Scheme 7.

net decomposition of starting material was observed only in the case of **3** as shown in Scheme 7 via a Norrish type II mechanism of the benzoylformate chromophore [24]. The apparent inertness of compounds **1**, **2** and **4** in benzene seems to suggest that the intended C–O bond homolysis does not occur. However, based on an early study of the intermolecular sensitized reactions [16], it is more likely that the cleavage of the C–O bond occurs as shown in Scheme 3. But the bond cleavage process is reversible, i.e.: the resulting benzylic radical was rapidly trapped by the simultaneously produced TEMPO radical. This equilibrium favors the starting material and only a steady state concentration of the radicals exists. This radical concentration is low enough so that the net disappearance of the starting material is not observed. Coupling between two benzylic radicals forming bibenzyl is not feasible when an equimolar amount of TEMPO radical also exists in the system [25], accounting for the absence of any photoproducts. The benzoylformate chromophore in **3** may undergo a Norrish type II γ-hydrogen abstraction in addition to sensitizing the C–O bond homolysis. The former leads to products shown in Scheme 7.

We irradiated compounds **1–4** in styrene-d_8 solvent in an attempt to trap the benzylic radical by addition to monomer molecules. The progress of the reaction was monitored by NMR experiments. Compounds **1–4** were reasonably stable when irradiated in styrene solution. Rapid quenching of the excited state of the chromophore by the styrene molecule [26] precluding the intramolecular sensitized C–O bond cleavage is likely the reason for the photostability of **1–4**.

However, the intended photosensitization reaction can be detected by transient experiments. Benzene solutions of **1–3** were subjected to laser flash photolysis on a setup descried earlier [19]. Transient absorptions characteristic of the chromophore's triplet excited state can be detected. Direct observation of the benzylic radical (maximum absorption at 320 nm [16]) was difficult because the triplet also strongly absorbs in this region of the spectrum. A typical example is shown in Fig. 1 for compound **3**. The transient absorption at 320 nm and 440 nm are due to the triplet state of the benzoylformate chromophore in agreement with an earlier study [24]. Traces monitored at both 320 and 440 nm (inserts) decays with the same lifetime (0.6 μs).

The transient absorption and the decay trace monitored at 640 nm after an acetonitrile solution (0.005 M) of **4** was subjected to laser flash are displayed in Fig. 2. The absorption at 320 nm grows while that at 640 nm decays away with the delay time. The absorption at 640 nm is assigned to the triplet state of the xanthone chromophore in agreement with the literature [27,28]. A lifetime of 0.24 μs was obtained for the triplet of **4** from the exponential fit of the decay trace at 640 nm. The decay trace monitored at 330 nm displayed a grow-decay pattern as shown in Fig. 3. The rate constant of this transient formation is $2.5 \times 10^7\ \mathrm{s}^{-1}$ and its decay rate constant is $7.0 \times 10^6\ \mathrm{s}^{-1}$ under the present conditions. The transient absorption maximizing at 320 nm was assigned to the benzylic radical. It is therefore obvious that the C–O

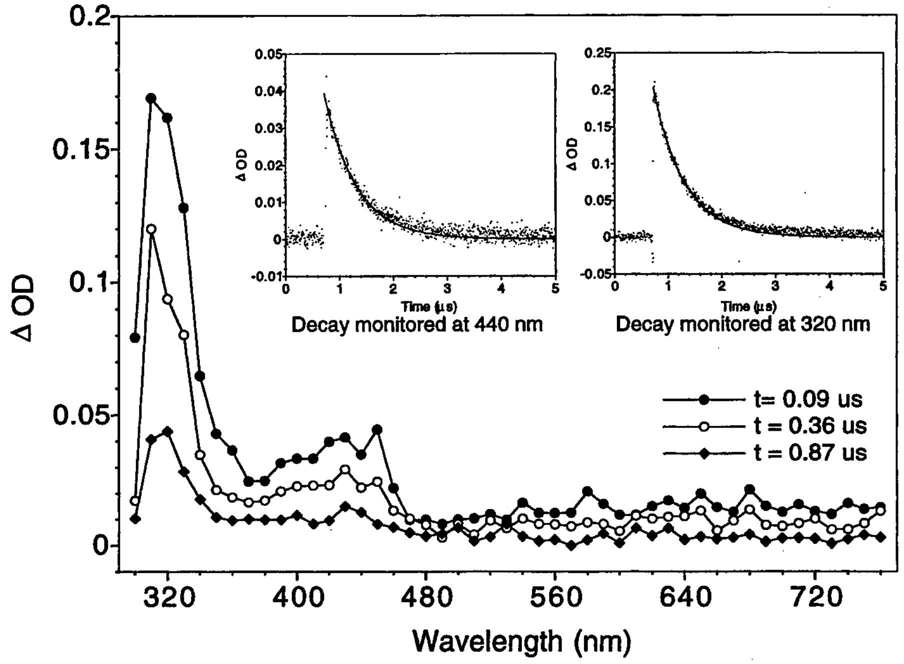


Fig. 1. Transient absorption spectra detected at different delay times after laser flash of a benzene solution (0.02 M) of compound **3**. Decay traces monitored at 320 nm (right) and 440 nm (left) are inserted.

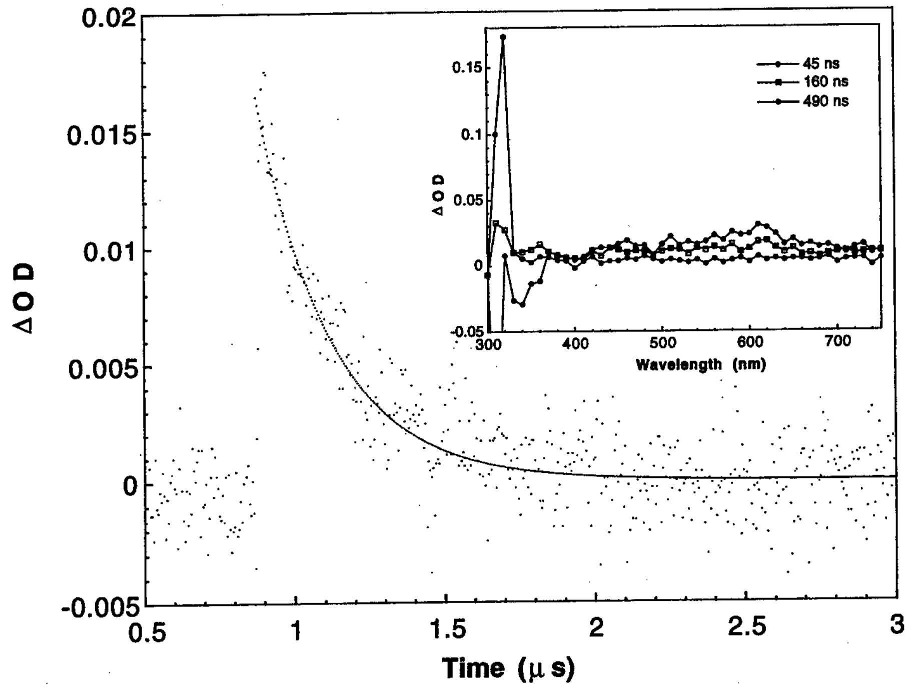


Fig. 2. Transient decay trace monitored at 640 nm after an acetonitrile solution of **4** (0.005 M) was laser flashed. Inserted are transient absorption spectra at different delay times.

bond homolysis occurred in compound **4**. We were unable to detect directly the benzylic radical in the reactions of **1**–**3**. This is in part due to the fact that the xanthone triplet in **4** absorbs away from the region where the benzylic radicals appear while the phenyl ketone chromophores in **1**–**3** absorbs strongly at shorter wavelengths. Furthermore, the triplet energy of the xanthone chromophore in **4** is higher than those of the phenylketone chromophores of **1**–**3** [16]. It is therefore likely that the C–O homolysis in **4** is more efficient than that in **1**–**3**.

The triplet lifetimes of **1**–**4** and those of the appropriate compounds containing the chromophore but no amino-ether moiety (as controls) are given in Table 1. Significant shortening of the triplet lifetime by the intramolecularly situated alkylated TEMPO moiety in **1**–**4** was observed compared to the control compounds. Since the experimental conditions are identical for the chromophore containing alkylated TEMPO compounds (**1**–**4**) and their corresponding controls, the shorter lifetime for **1**–**4** has to be attributed to the intramolecular quenching of the triplet by the TEMPO moiety. This quenching process may or may not lead to a significant C–O homolysis in **1**–**3**. The bond cleavage process was directly detected in **4**.

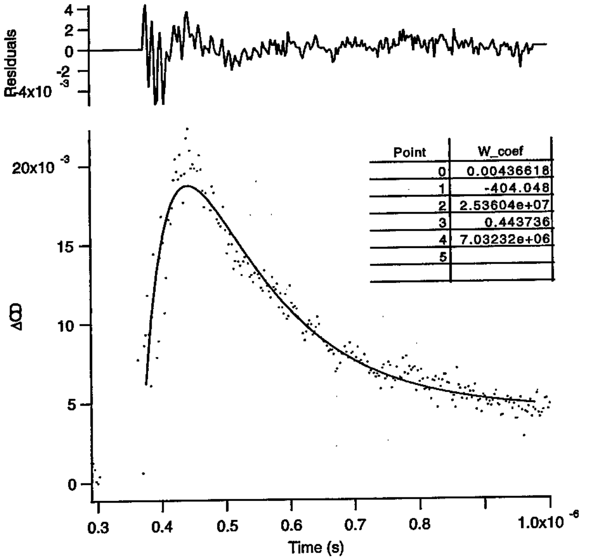
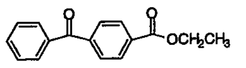


Fig. 3. Transient decay trace monitored at 330 nm after an acetonitrile solution of **4** (0.005 M) was laser flashed (lower). Upper portion is the residual showing the quality of the bimodal fit.

Table 1

Triplet lifetimes of **1**–**4** and the control compounds under identical experimental conditions Ref. [29].



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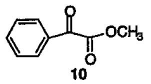

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Compound	τ_T (μs)	Controls	$\tau_{T\ \mathrm{Control}}$ (μs)
1	0.63	**9**	5[a]
2	0.64	**9**	5[a]
3	0.60	**10**	1.24[b]
4	0.24	Xanthone	17.9[c]

[a] Data from Ref. [29].

[b] Data from Ref. [29].

[c] Data in ethanol from Ref. [27].

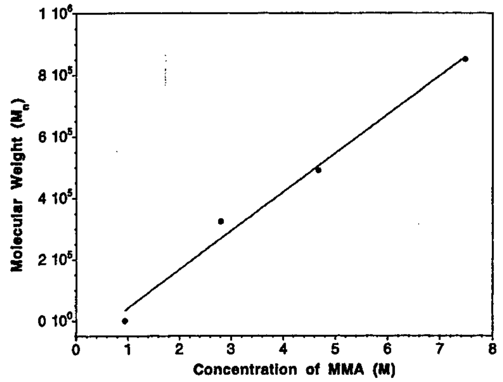
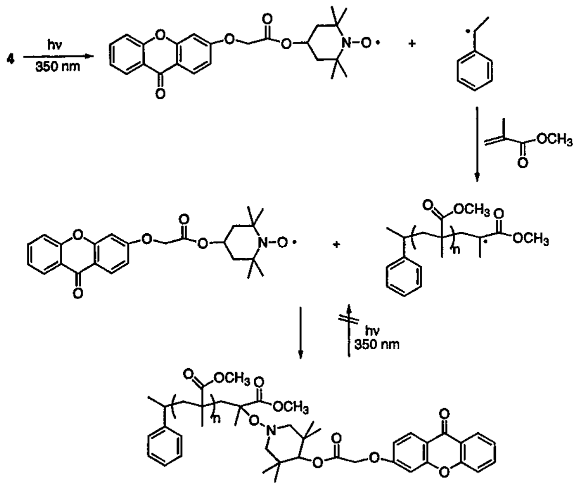


Fig. 4. Molecular weight of poly(methyl methacrylate) produced using 0.005 M of **4** as photoinitiator with different monomer concentration in acetonitrile.

3.3. Controlled polymerization

As indicated earlier, employing **1–4** as photoinitiators for styrene polymerization is difficult due to the rapid quenching of the excited chromophore by the styrene. We used **4** as photoinitiator for methyl methacrylate polymerization because controlled polymerization of acrylate is of recent research interest [18]. Solutions in acetonitrile containing various concentrations of methyl methacrylate and a constant amount of the initiator **4** (0.005 M) were prepared. The mixtures were irradiated under inert atmosphere for 12 h. At the end of the irradiation, the mixture was poured into methanol and the resulting polymer (if any) was collected and dried to constant weight. The molecular weights of the polymer show a close relation with the monomer concentration as displayed in Fig. 4.

This observation is in good agreement with controlled (not “living”) polymerization reactions initiated by other photoinitiators operating by similar mechanism [18]. As shown in Scheme 8, initially, a substituted TEMPO radical and the initiating benzylic radical were formed when **4** was irradiated. The benzylic radical subsequently adds to the methyl methacrylate monomer to invoke a chain reaction, the length of which depends on the concentration of the monomer presented in the system. The propagating radical was trapped by the TEMPO radical and terminates the reaction. The resulting polymer is not photoreactive under the irradiation conditions. This is likely due to the unfavorable energy demands needed to break the C–O bond producing an alkyl radical [30] rather than a benzylic radical as in the case of **4**. The polymer is therefore unreactive in initiating further polymerization of the monomer, and the reaction is not a “living” process. Nevertheless, the molecular weight and the polydispersity of the polymer produced by controlled photopolymerization can be successfully managed by varying the concentrations of the monomer [18].



Scheme 8.

4. Conclusions

Several chromophore containing TEMPO compounds were synthesized, and their photochemistry and photophysics studied. Different degrees of intramolecularly sensitized C–O bond homolysis were observed when the chromophore was altered. Direct detection of the homolysis process by laser flash photolysis was possible in the xanthone containing compound **4**. Controlled polymerization of methyl methacrylate was observed when **4** was employed as photoinitiator.

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